The present invention relates to compositions and methods for finishing surfaces of cadmium and zinc and alloys thereof.

The term "zinc surfaces" as used herein refers to surfaces of zinc and zinc-base alloy articles and other metallic articles having a coating of zinc or zinc-base alloy such as produced by hot-dipping or electroplating.

The term "cadmium surfaces" as used herein refers to surfaces of cadmium and cadmium-base alloy articles and other metallic articles having a coating of cadmium or cadmium-base alloy such as produced by electroplating.

It is the aim of the present invention to provide a novel composition and method for finishing zinc surfaces and cadmium surfaces which is relatively simple in operation and provides protection thereto.

Another aim is to provide a simple and effective dilute single-dip composition and method for treating surfaces of zinc and zinc-base alloys to impart a bright finish thereto.

It is also an aim to provide a single-dip composition and method for surface-treating zinc and zinc-base alloys which give a high degree of protection in a bright or bright iridescent finish.

A further aim is to provide a self-contained dry powder composition for addition to water which will yield a bath for finishing zinc surfaces and cadmium surfaces to impart protection thereto.

It has now been found that the foregoing and related aims can be readily attained by immersing the zinc or cadmium workpiece in a dilute aqueous bath containing essentially molybdate ions, nitrate ions, and an activating ion selected from the group consisting of fluoride and sulfate, the bath having a pH of about 0.5-2.2 and preferably about 0.9-1.5. A leveling agent such as borate ion or acetate ion may also be incorporated to control the bath operation and produce increased clarity. The bath is maintained at ambient temperatures, and the workpiece is immersed therein for a period of about five to thirty seconds, preferably with agitation.

Generally, the dilute baths of the present invention contain essentially about 0.2-6.5 grams per liter molybdate ion, 4.0-100.0 grams per liter of nitrate ion, 0.1-15.0 grams per liter of activating ion selected from the group consisting of fluoride and sulfate, and up to about 4.0 grams per liter of a leveling ion selected from the group consisting of borate and acetate. The nitrate ion should be maintained at a weight ratio relative to the molybdate ion in excess of about 10:1 to obtain desirable brightening but less than about 40:1 for desirable corrosion protection, and preferably on the order of 15-30:1.

By use of certain weight ratios of activating ion to molybdate ion, it has been found that good brightening action upon zinc can be readily attained through varying concentrations of the two components in the bath. When using the fluoride ion, it has been found desirable to utilize a fluoride to molybdate ion weight ratio of about 1.3-3.1, and preferably about 1.4-1.8:1. When using the sulfate ion, it has been found desirable to utilize a sulfate to molybdate weight ratio of about 0.5-2.0:1, and preferably about 0.7-1.2:1. Use of both sulfate and fluoride ions in a common bath formulation has been found generally to reduce the brightness of finish and, accordingly, only one of the activating ions should be employed for optimum results. In practice, the fluoride ion baths appear to provide greatest brightness.

Levelling agents are desirably incorporated in the bath for pH control and control of the rate of bath action to achieve optimum brightening without the need for a critical control of times and temperatures. As little as 0.05 gram per liter will produce a beneficial effect, and amounts up to about one-third the weight of molybdate and activating ion, or about 4.0 grams per liter, may be utilized, although the corrosion protection will generally be reduced by increasing concentration of the leveling ion. Accordingly, it is preferred to use only about 0.1-0.8 gram per liter for optimum brightening and corrosion protection. Borates and acetates have proven satisfactory as leveling agents.

The baths of the present invention have proven highly effective in providing both brightness and corrosion protection upon zinc surfaces, the brighter finishes surprisingly demonstrating good corrosion protection, and the dull finishes generally exhibiting considerably lesser or no significant degree of corrosion protection as measured by the lead acetate test. Although the present invention may be utilized to produce a bright finish upon cadmium surfaces under closely controlled conditions, generally there is produced a finish which varies from a cloudy film or yellow or blue iridescent to dull grey in appearance but which does provide some measure of corrosion protection. Accordingly, the present invention in its preferred aspect is directed to the treatment of zinc surfaces.

The several ions can be added to the bath as the acid or as salts which are soluble in water or acid solutions. However, since molybdate acid is relatively insoluble in both water and acid solutions, the alkali metal molybdates and particularly sodium molybdate have been advantageously employed.

Specific examples of finishing baths in accordance with the present invention and utilizing nitric acid are as follows:

<table>
<thead>
<tr>
<th>FLUORIDE ION</th>
<th>Range</th>
<th>Optimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali Metal Molybdate</td>
<td>0.25-4.0 g</td>
<td>1.0 g</td>
</tr>
<tr>
<td>Alkali Metal Biphosphate</td>
<td>0.05-12.0 g</td>
<td>2.0 g</td>
</tr>
<tr>
<td>Nitric Acid, 45% Solution</td>
<td>0.5-10.0 cc</td>
<td>To 1.0 liter</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td>To 1.0 liter</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SULFATE ION</th>
<th>Range</th>
<th>Optimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali Metal Molybdate</td>
<td>0.5-8.0 g</td>
<td>2.0 g</td>
</tr>
<tr>
<td>Alkali Metal Bisulfate</td>
<td>0.5-8.0 g</td>
<td>2.0 g</td>
</tr>
<tr>
<td>Nitric Acid, 45% Solution</td>
<td>0.5-10.0 cc</td>
<td>To 1.0 liter</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td>To 1.0 liter</td>
</tr>
</tbody>
</table>

By use of sufficient quantities of acidic salts to provide a variety of the component ions, a self-contained dry powder formulation can be prepared which will form the desired bath upon addition to water. Alkali metal-hydrogen and ammonium-hydrogen salts of fluoride and sulfate have been particularly useful as has urea nitrate for this purpose.

Generally, a dry powder formulation for addition to water contains essentially about 2.0-8.0 percent by weight alkali metal molybdate; 1.0-40.0 percent by weight of an 1 A drope of an aqueous solution containing 5 percent by weight lead acetate is placed upon the surface and the time noted until the spot turns black. Generally 10 seconds is indicative of a high measure of protection since an untreated panel will turn black immediately.
activating agent having an anion selected from the group consisting of sulfates and fluorides and a positive radical selected from the group consisting of alkali metal-hydrogen, alkali metal and ammonium-hydrogen; up to 8.0 percent by weight of a solid leveling agent having an anion selected from the group consisting of acetate and borate and a cation selected from the group consisting of hydrogen, alkali metal and ammonium; and 50.0–95.0 percent by weight of a nitrate compound having a cation selected from the group consisting of alkali metal, urea and ammonium, at least one of said components being sufficiently acidic in nature to provide a pH of 0.5–2.2 upon addition of the composition to water in sufficient quantity to provide about 0.25–8.0 grams per liter of alkali metal molybdate.

Specific examples of self-contained dry powder compositions in accordance with the present invention are as follows:

**FLUORIDE ION**

<table>
<thead>
<tr>
<th>Range, Grams</th>
<th>Optimum, Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali Metal Molybdate</td>
<td>2.0–7.0</td>
</tr>
<tr>
<td>Alkali Metal-Hydrogen Fluoride</td>
<td>0.2–2.0</td>
</tr>
<tr>
<td>Boric Acid</td>
<td>Up to 5.0</td>
</tr>
<tr>
<td>Urea Nitrate</td>
<td>0.10–0.05</td>
</tr>
</tbody>
</table>

**SULFATE ION**

<table>
<thead>
<tr>
<th>Range, Grams</th>
<th>Optimum, Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali Metal Molybdate</td>
<td>2.0–3.0</td>
</tr>
<tr>
<td>Alkali Metal-Hydrogen Sulfate</td>
<td>5.0–40.0</td>
</tr>
<tr>
<td>Boric Acid</td>
<td>Up to 10.0</td>
</tr>
<tr>
<td>Alkali Metal Nitrate</td>
<td>50.0–65.0</td>
</tr>
</tbody>
</table>

Either type of dry powder formulation may be added to water in amounts sufficient to provide the desired concentration of molybdate ion; i.e., about 0.2–6.5 grams per liter or about 0.25–8.0 grams per liter of alkali metal molybdate. Generally, this will require about 10.0–100.0 grams of powder formulation per liter of water. The pH of the resultant bath will vary with the concentration of the acidic component within the powder formulation and within the bath. Generally, the baths of the present invention are employed at ambient temperatures of about 65–90 degrees Fahrenheit and require immersion for short periods of about five to thirty seconds, preferably with mild agitation. However, lower elongated temperatures of up to about 120 degrees Fahrenheit may be used, although with lesser control and shorter dip times. The workpieces are then rinsed in cold water.

Since the baths are corrosive, suitable tanks and handling equipment should be employed to avoid contamination such as rigid polyvinyl chloride or glass fiber reinforced resin.

Exemplary of the efficacy of the present invention are the following specific examples wherein test panels 2 inches x 3 inches were electroplated with zinc or cadmium and immersed in the several formulations under equivalent conditions of temperature, time and agitation.

**Example 1**

A bath was prepared by admixing 2.0 grams sodium fluoride, 1.35 grams sodium molybdate, 0.14 gram boric acid and 21.0 cc. of 42° Baume nitric acid in water to make 1.0 liter. The pH of the bath was measured at 1.35 using a reference solution of pH 1.1.

A steel test panel 2 inches x 3 inches having an electroplated zinc coating thereon was immersed in the bath at room temperature for about twelve seconds with agitation and then rinsed in cold water. The resultant finish was bright and free from iridescence. A drop of 5.0 percent by weight lead acetate solution did not turn the finish black for over twenty seconds, indicating a high degree of corrosion protection.

**Example 2**

A bath was prepared by dissolving in one liter of water 2.0 grams of sodium-hydrogen fluoride, 1.35 grams of sodium molybdate, and 30.0 grams of urea nitrate. The resultant pH was 1.8.

A zinc-plated steel test panel 2 inches x 3 inches was immersed therein at room temperature for about twelve seconds and then rinsed. The resultant finish was bright and gave a value of twenty seconds in the lead acetate test, indicating a high degree of corrosion protection.

**Example 3**

A bath was prepared by dissolving in one liter of water 2.0 grams of sodium-hydrogen fluoride, 1.35 grams of sodium molybdate, and 30.0 grams of urea nitrate. The resultant pH was 1.8.

A zinc-plated steel test panel 2 inches x 3 inches was immersed therein at room temperature for about twelve seconds and then rinsed in cold water. The panel finish was bright and gave a surprisingly high test value of fifty-five seconds in the lead acetate test, indicating a very high degree of corrosion protection.

The addition of a further 10.0 grams of sodium nitrate produced a bath having a pH of 1.8 and resulted in a milky or cloudy finish upon the test panel. However, the value in the lead acetate test was not diminished.

**Example 4**

A bath was prepared by dissolving in one liter of water 5.6 grams of sodium bisulfate, 1.35 grams of sodium molybdate and 20.0 grams of sodium nitrate. The resultant pH was 1.0.

A zinc-plated steel test panel 2 inches by 3 inches was immersed therein at room temperature with agitation for about twelve seconds and then rinsed in cold water. The resultant finish was bright blue and gave a value of fifteen seconds in the lead acetate test, indicating a high degree of corrosion protection.

**Example 5**

A bath was prepared by dissolving 2.1 grams of sodium bisulfite, 1.35 grams of sodium molybdate, 0.14 gram of boric acid and 20.0 grams of urea nitrate in one liter of water.

A cadmium-plated steel panel 2 inches x 3 inches was immersed therein with agitation for about ten seconds at room temperature and then rinsed in water. The resultant finish was of yellowish, slightly iridescent hue and gave a value of six seconds in the lead acetate test, indicating a fair measure of corrosion protection.

Thus, it can be seen from the foregoing detailed specification and specific examples that the present invention provides a novel composition and method for finishing zinc and cadmium surfaces to provide protection therefor which is relatively simple in operation. The compositions of the present invention provide a single-dip bath for surface treating zinc and zinc-base alloys to provide a bright finish therefor which will give a high degree of corrosion protection. According to one aspect of the present invention, it is possible to provide a self-contained dry powder composition for addition to water to yield a bath for finishing zinc and cadmium surfaces to impart protection thereon.
Having thus described the invention, I claim:

1. A bath for treating zinc surfaces and cadmium surfaces comprising a dilute aqueous acid solution containing essentially about 0.2-6.5 grams per liter molybdate ion, 4.0-100.0 grams per liter nitrate ion, and 0.1-15.0 grams per liter of an activating ion selected from the group consisting of fluoride and sulfate, said solution having a pH of about 0.5-2.2.

2. The bath in accordance with claim 1 wherein said solution contains a leveling ion selected from the group consisting of borate and acetate in an amount of about 0.05-0.5 grams per liter and not more than one-third the weight of the molybdate and activating ions.

3. The bath in accordance with claim 1 wherein the weight ratio of nitrate ion to molybdate ion is 10-40:1.

4. The bath in accordance with claim 1 wherein the activating ion is fluoride and the fluoride to molybdate weight ratio is 1:3-10:1.

5. The bath on accordance with claim 1 wherein the activating ion is sulfate and the sulfate to molybdate weight ratio is 0.5-2:1.

6. The bath in accordance with claim 1 wherein the pH is about 0.9-1.5.

7. A bath for treating zinc surfaces comprising a dilute aqueous solution containing essentially 0.25-4.0 grams per liter of alkali metal molybdate, fluoride ion in a fluoride to molybdate weight ratio of about 1.4-1.8:1, and nitrate ion in a nitrate to molybdate weight ratio of about 10-40:1, said solution having a pH of about 0.9-1.5.

8. A bath for treating zinc surfaces comprising a dilute aqueous solution containing essentially 0.5-8.0 grams per liter alkali metal molybdate, sulfate ion in a sulfate to molybdate weight ratio of about 1.5-2:1, and nitrate ion in a nitrate to molybdate weight ratio of about 10-40:1, said solution having a pH of about 0.9-1.5.

9. A bath for treating zinc surfaces comprising a dilute aqueous solution containing essentially 0.25-4.0 grams per liter alkali metal molybdate, 0.5-12.0 grams per liter alkali metal-hydrogen fluoride and 4.5-75.0 cc. per liter nitric acid, said bath having a fluoride ion to molybdate ion ratio of about 1.4-1.8:1 and a nitrate ion to molybdate ion ratio of about 15-30:1, said bath having a pH of about 0.9-1.5.

10. A self-contained dry powder formulation for addition to water to provide a bath for treating zinc surfaces and cadmium surfaces to impart corrosion protection thereto, said formulation containing essentially about 2.0-8.0 percent by weight of a water-soluble solid leveling agent having an anion selected from the group consisting of sulfates and fluorides and a positive radical selected from the group consisting of alkali metal-hydrogen, alkali metal and ammonium-hydrogen; up to 8.0 percent by weight of a water-soluble solid leveling agent having an anion selected from the group consisting of acetate and borate and a cation selected from the group consisting of hydrogen, alkali metal and ammonium; and 50.0-95.0 percent by weight of a water-soluble nitrate compound having a cation selected from the group consisting of alkali metal, urea and ammonium, at least one of said components being sufficiently acidic in nature to provide a pH of 0.5-2.2 upon addition of the composition to water in sufficient quantity to provide about 0.25-8.0 grams per liter of alkali metal molybdate.

11. The dry powder formulation in accordance with claim 10 wherein the pH produced by said acidic component upon addition to water is 0.9-1.5.

12. The dry powder formulation in accordance with claim 10 wherein said nitrate compound is urea nitrate.

13. The dry powder formulation in accordance with claim 11 wherein said nitrate compound is in an amount providing a nitrate ion to molybdate ion ratio in the formulation of 10-40:1.

14. The dry powder formulation in accordance with claim 10 additionally containing up to 8.0 percent by weight of a water-soluble solid leveling agent having an anion selected from the group consisting of acetate and borate and a cation selected from the group consisting of hydrogen, alkali metal and ammonium.

15. The dry powder formulation in accordance with claim 10 wherein the weight ratio of nitrate ion to molybdate ion is 15-30:1.

16. The method of treating zinc surfaces and cadmium surfaces to impart corrosion protection thereto comprising providing a dilute aqueous acid solution containing essentially about 0.2-6.5 grams per liter molybdate ion, 4.0-100.0 grams per liter nitrate ion, and 0.1-15.0 grams per liter of an activating ion selected from the group consisting of fluoride and sulfate, said solution having a pH of about 0.5-2.2; maintaining said solution at a temperature of about 60-120 degrees Fahrenheit; and immersing therein a workpiece having a surface selected from the group consisting of zinc surfaces and cadmium surfaces for a period of five to thirty seconds to develop corrosion protection thereon.

17. The method in accordance with claim 16 wherein said solution has a pH of 0.9-1.5.

18. The method in accordance with claim 16 wherein the weight ratio of nitrate ion to molybdate ion is 10-40:1.

19. The method in accordance with claim 16 wherein said workpiece has a zinc surface and said solution provides a bright surface finish thereto.

References Cited in the file of this patent

UNITED STATES PATENTS

2,186,579 Dupernell et al. Jan. 9, 1940
2,377,593 Bunie June 5, 1945
2,904,413 Hampel Sept. 15, 1959
2,904,414 Ostrander et al. Sept. 15, 1959
3,072,516 Bellinger et al. Jan. 8, 1963